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## Hydrogen Bridges

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THE univalence of hydrogen has long been a cardinal principle of chemistry. However, the valence of an atom is not always the same as the number of bonds connecting it to other atoms. This has been evident since G. N. Lewis, elucidating his theory of valence, showed that electron-pair bonds can be formed not only by the union of two atoms holding single unpaired electrons but also by the union of an atom containing a 'lone pair' of electrons to another atom capable of adding an electron pair to its valence shell—

$$\begin{aligned} A\cdot \; + \; \cdot B &\longrightarrow A{:}B \\ A \; + \; {:}B &\longrightarrow A{:}B \end{aligned}$$

The existence of most 'secondary-valence' compounds is attributable to reactions of this latter type, and the known crystal structures of hundreds of inorganic compounds can be accounted for only by assuming that such reactions occur during the crystallization process.

Until recently it has not been generally realized that a hydrogen atom already bonded to one other atom can, under certain circumstances, become bonded to a second atom in the following way—

$$X{:}H \; + \; {:}Y \longrightarrow X{:}H{:}Y$$

The evidence indicating this, however, is now so conclusive that there can no longer be any reasonable doubt of the existence of 'hydrogen bridges' or 'hydrogen bonds,' as these structures have come to be called.

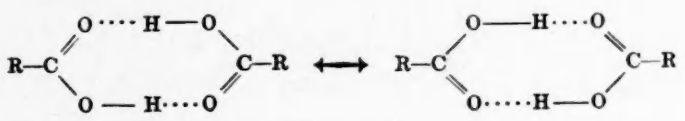
Perhaps the most definite proof comes from investigations of the structures of crystals and liquids by x-ray diffraction, and of gas molecules by electron diffraction. These studies show hydrogen atoms to be between pairs of electronegative atoms in many cases. Raman and infrared spectra also furnish important evidence. The association of organic acids, alcohols, etc., in solution and in the vapor state, indicated by cryoscopic, vapor-density, and other measurements, closely follows the requirements of the hydrogen-bridge theory. Further corroboration comes from studies of solubilities and of heats of mixing of liquids.

Hydrogen forms strong bridges between atoms of relatively few elements —namely, F, O, N, and, under very special circumstances, C. If bridges involving other elements exist at all, they are relatively weak.

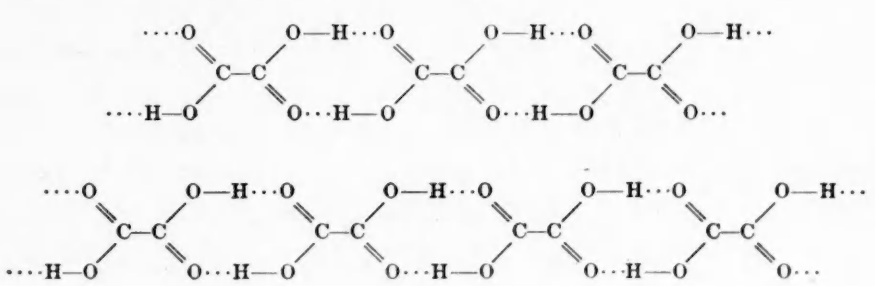
The energy required to break a hydrogen bridge is about 6 or 7 kilocalories per mole, in the cases on which data are available. A hydrogen bridge is thus roughly one-tenth as strong as an ordinary single bond in an organic molecule. The distance between the atomic nuclei at the bridge-ends is about 2.5 to 2.8 Å.,

that is, about 2½ times the length of a CH, NH, or OH bond. There is reason to believe that hydrogen bridges are sometimes symmetrical, with the hydrogen oscillating about the midpoint of the bridge; and sometimes unsymmetrical—the hydrogen remaining closer to one terminal atom than to the other, even though both are of the same element. If a hydrogen bridge is part of a resonating ring or long-chain system, its stability seems to be somewhat greater than otherwise.

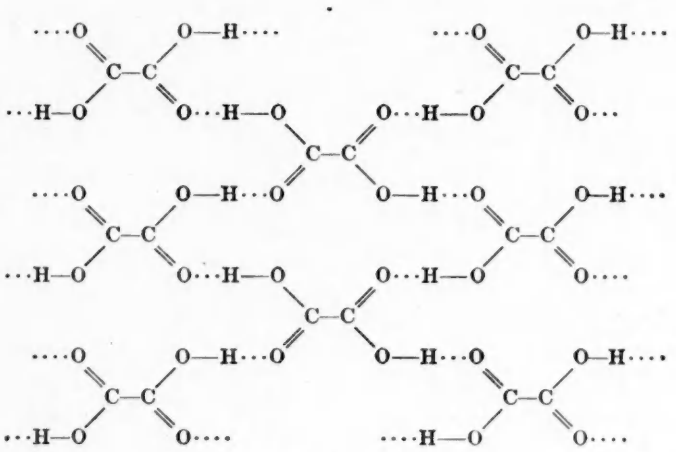
The dimerization of monocarboxylic acids in nonaqueous solutions and in the solid and liquid, and sometimes gaseous, states is now known to be due to hydrogen-bridge formation. The 'double' molecule can be considered to be resonating between two structures:



Because of such bridge formation, the dicarboxylic acids are solids at ordinary room temperatures. The atomic distribution in the two crystalline forms of anhydrous oxalic acid may be diagrammatically represented as follows—



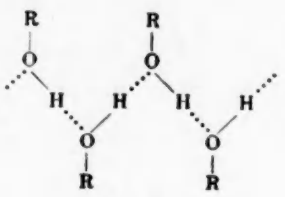
*β form*



*α form*

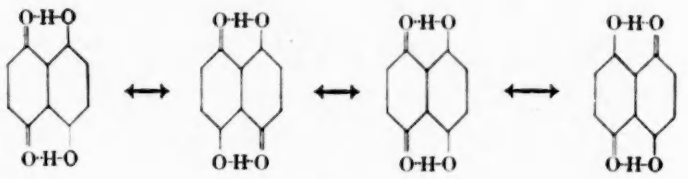
In the presence of water, this and similar acids form hydrates in which the water oxygens and the carboxyl oxygens are connected to each other through hydrogen bridges.

Hydrogen-bridge formation is also responsible for the association of alcohols—

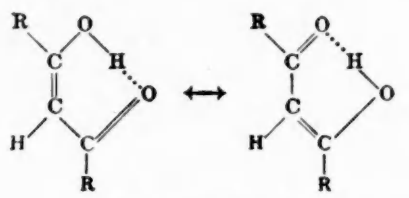


In ice, each oxygen atom is held to four neighbors through hydrogen bridges. In liquid water, this is the preferred type of arrangement; because of the heat motions of the atoms, however, the bridge connections are continually being broken and new ones formed.

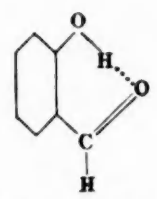
Intramolecular OHO bridges occur in the following compounds and in many other substances:



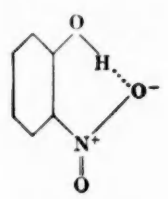
*naphthazarine*



*acetylacetone*

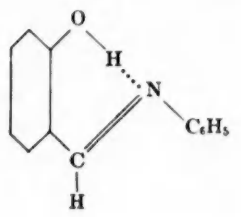


*salicylaldehyde*



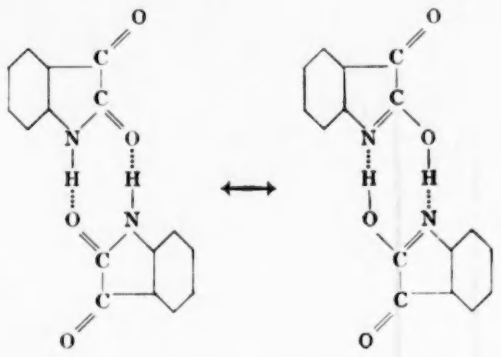
*o-nitrophenol*

Salicylaldehydeanil, which is structurally represented at the right, is an example of those substances containing intramolecular NHO bridges.



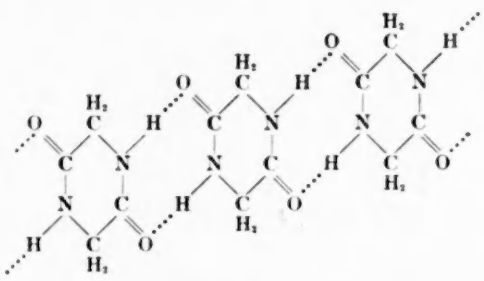
Isatin is a typical il-

lustration of NHO bridges connecting pairs of molecules—



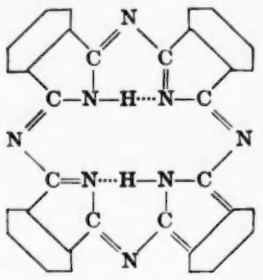
Many loose molecular compounds, such as those between pyridine and various phenols, may be attributed to similar bridge formations.

In diketopiperazine, NHO bridges produce molecular chains—



It seems probable that the polypeptide chains of proteins are held together in a comparable manner.

A very interesting example of NHN bridges is afforded by the molecule of phthalocyanine, which, according to the x-ray data, may be considered as resonating between the structure shown at the right and several others that differ only in the distribution of the bonds.



Hydrogen bridges that connect a carbon atom to one of another element are relatively rare. There is evidence, however, of bridge formation by the CH hydrogen atom in chloroform, formic acid, and hydrocyanic acid. For example, the molecular complexes which are formed by chloroform with ether and acetone are probably held together in this way.

The compounds mentioned in this article, although typical, are but a few of those now known to contain hydrogen bridges. For a more comprehensive review, reference may be made to Huggins, *J. Org. Chem.* *1*, 407 (1936). Knowledge of this subject has been greatly extended recently, yet the full significance of hydrogen-bridge formation and its importance in determining both the physical and the chemical properties of many substances are only just beginning to be realized.

## Changes in Prices of Eastman Organic Chemicals

**Effective subsequent to publication of List No. 30—May 15, 1939**

| | | | | |
|---|---|---|---|---|
| P 597 | Acenaphthene (90-95%) (Pract.) | 1 kg. | $ 3.25 | E |
| 29 | Anthranilic Acid MP 143.5-144.5° | 1 kg. | 5.50 | E |
| 33 | Benzidine MP 126-127° | 500 g. | 15.00 | D |
| P 2023 | 2,5-Diaminotoluene Sulfate (Pract.) | 1 kg. | 6.60 | E |
| P 583 | Fumaric Acid (Pract.) MP 293-295° | 1 kg. | 3.25 | E |
| 1366 | Furoic Acid MP 131-132° | 100 g. | 2.50 | C |
| T 1366 | Furoic Acid (Techn.) | 1 kg. | 4.50 | G |
| 575 | Hydrazine Sulfate | 100 g. | 3.00 | C |
| 3025 | α-Hydroxy-iso-butyric Acid MP 78-79° | 500 g. | 5.00 | D |
| P 2416 | β-Methylnaphthalene (Pract.) MP 29-33° | 500 g. | 3.25 | D |
| 1460 | Phosphotungstic Acid | 500 g. | 12.00 | D |
| 3472 | Pimelic Acid MP 103-105° | 1 g. | .95 | A |
| P 1456 | Thiodiphenylamine (Pract.) MP 178-180° | 500 g. | 10.00 | D |
| P 459 | iso-Valeric Acid (Pract.) BP 170-180° | 1 kg. | 9.00 | E |

# New Eastman Organic Chemicals

| | | | |
|---|---|---|---|
| P 4101 | Aluminum iso-Propoxide (Pract.) | 500 g. | $12.50 D |
| P 4867 | 2-Amino-5-chlorobenzoic Acid (Pract.) MP 197-200° | 500 g. | 11.00 D |
| P 4808 | 5-Amino-2-naphthol Hydrochloride (Pract.) | 100 g. | 8.00 C |
| 4812 | Benzothiazole BP 117-118°/20 mm. | 100 g. | 8.00 C |
| 4859 | p-Bromobenzyl Bromide MP 61-62° | 100 g. | 8.00 C |
| P 4868 | 2-Bromo-4-*tert*.-butylphenol (Pract.) BP 123-125°/14 mm. | 500 g. | 5.25 D |
| P 4869 | 2-Bromo-4-phenylphenol (Pract.) | 500 g. | 3.25 D |
| 4810 | m-Chloroacetanilide MP 77-78° | 100 g. | 4.00 C |
| P 4862 | 4-Chlorobenzophenone (Pract.) MP 64-70° | 500 g. | 5.00 D |
| P 4826 | 1-Chloro-1-nitropropane (Pract.) 86% boiling at 142-145° | 1 kg. | 2.50 E |
| 4858 | 2-Chloro-5-nitropyridine MP 106.5-108° | 100 g. | 10.00 C |
| 4870 | β-Chlorophenetole MP 24-25.5° | 500 g. | 6.00 D |
| 4815 | 2,4,6-Collidine BP 167-169° | 500 g. | 6.00 D |
| 4847 | 2,6-Diaminopyridine Monohydrochloride MP 79-82° | 100 g. | 5.50 C |
| 4853 | Dihydroxyacetone | 1 g. | 2.00 O |
| P 4864 | 1,1-Diphenylethane (Pract.) BP 137-139°/14 mm. | 1 kg. | 3.00 E |
| P 4830 | Ethyl Oxalacetate (Sodium Salt) (Pract.) | 1 kg. | 3.00 E |
| 4828 | *d*-Glucoascorbic Acid·1$H_2O$ | 100 g. | 6.00 C |
| P 417 | p-Hydroxyazobenzene (Pract.) MP 151-153° | 500 g. | 5.50 D |
| 4846 | 2-Hydroxy-5-nitropyridine MP 187-189° | 100 g. | 8.00 C |
| P 4863 | 2-Hydroxypyridine (Pract.) MP 100-106° | 100 g. | 7.50 C |
| 4814 | 2,3-Lutidine BP 158-160° | 500 g. | 6.00 D |
| 4820 | 2,6-Lutidine BP 141-142.5° | 500 g. | 6.00 D |
| 4629 | Methyl β-Bromopropionate BP 58-60°/12 mm. | 100 g. | 4.00 C |
| 3083 | p-Methylcyclohexanone BP 169-170.5° | 100 g. | 4.50 C |
| 4835 | N-(1-Naphthyl)-ethylenediamine Dihydrochloride | 1 g. | 1.25 O |
| 4837 | β-Nitroalizarin MP 242-244° dec. | 1 g. | .75 A |
| 4817 | n-Nonyl Bromide BP 101.5-103.5°/17 mm. | 100 g. | 15.00 C |
| 4860 | Phenothioxin MP 56-58° | 500 g. | 6.00 D |
| P 4861 | β-Phenoxyethyl Alcohol (Pract.) BP 126-127.5°/15 mm. | 500 g. | 3.00 D |
| 4708 | 1,2,3,4-Tetrahydroquinoline BP 125-128°/18 mm. | 10 g. | 1.50 A |
| P 4833 | Trimethylol Aminomethane (Pract.) | 1 kg. | 2.75 E |
| P 4840 | Trimethylol Nitromethane (Pract.) | 1 kg. | 2.25 E |
| 4844 | n-Undecyl Alcohol MP 10-12° | 100 g. | 7.00 C |
| 4849 | n-Undecyl Bromide BP 138-141°/20 mm. | 100 g. | 9.50 C |